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(54) PHOTOCATALYTIC COATING FLUID CONTAINING TITANIUM OXIDE AND ITS MANUFACTURING METHOD AND TITANIUM OXIDE PHOTOCATALYTIC STRUCTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To prepare a photocatalytic coating fluid capable of obtaining a photocatalytic film having high transparency and, at the same time, no fine cracks which have been difficult to meet.

SOLUTION: The photocatalytic coating fluid forms a thin film having titanium oxide as the major component on a base material and comprises 0.1-10 wt.% titanium oxide (TiO<sub>2</sub>) having an average particle size of 50-120 nm and a crystallite diameter of 6-18 nm, 0.1-10 wt.% silica compound (SiO<sub>2</sub>), and ≥60 wt.% alcoholic solvent.

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CLAIMS

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[Claim(s)]

[Claim 1] Titanium oxide content photocatalyst coating liquid characterized by including the titanium oxide (TiO<sub>2</sub>) whose mean particle diameter is 50nm - 120nm and 6-18nm of diameters of microcrystal, and including an alcoholic solvent for a silica compound (SiO<sub>2</sub>) 60% of the weight or more 0.1 to 10% of the weight 0.1 to 10% of the weight in the photocatalyst coating liquid which makes the thin film which uses titanium oxide as a principal component form on a base material.

[Claim 2] Titanium oxide content photocatalyst coating liquid according to claim 1 whose pH is two or more in said titanium oxide content coating liquid, including an organic acid 0.005 to 5% of the weight.

[Claim 3] Titanium oxide content photocatalyst coating liquid according to claim 1 or 2 whose silica compounds are alkoxysilane or its condensate, and hydrolyzate.

[Claim 4] The manufacture approach of the titanium oxide content photocatalyst coating liquid characterized by mixing the titanium oxide and the silica compound whose mean particle diameter is 50nm - 120nm and crystal particle diameter of 6-18nm, and an alcoholic solvent in the manufacture approach of coating liquid of making the thin film which uses titanium oxide as a principal component forming on a base material so that it may become about a silica compound (SiO<sub>2</sub>) and may become 60 % of the weight or more about an alcoholic solvent 0.1 to 10% of the weight 0.1 to 10% of the weight in titanium oxide (TiO<sub>2</sub>).

[Claim 5] The manufacture approach of the titanium oxide content photocatalyst coating liquid according to claim 4 characterized by preparing pH of titanium oxide content photocatalyst coating liquid so that it may be set to 2-12.

[Claim 6] The photocatalyst structure which applied the titanium oxide content photocatalyst coating liquid of claim 1-3 given in any 1 term to the base material through the glue line.

[Claim 7] The photocatalyst structure according to claim 6 which is the glue line in which said glue line contained acrylic resin and silicon.

[Claim 8] The photocatalyst structure according to claim 7 whose silicone content in said glue line is 5 - 50 % of the weight.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] About the titanium oxide photocatalyst structure which used the coating liquid concerned for the titanium oxide content photocatalyst coating liquid which uses the photocatalyst effectiveness of titanium oxide and is used for harmful matter removal of NOX etc., deodorization, antifouling, antibacterial, etc., and its manufacture approach list, even if this invention has few cracks of the film at the time of spreading and they use it as a thick film especially, it relates to the titanium oxide content photocatalyst coating liquid which gives the film with high transparency, and its manufacture approach.

[0002]

[Description of the Prior Art] The titanium oxide photocatalyst is known for effectiveness, such as harmful matter removal of NOX etc., deodorization, antifouling, and antibacterial, being shown by the chemical reaction which absorbs and starts ultraviolet rays. By the way, in order to make the photocatalyst effectiveness discover industrially, it is required on a base material to make a photocatalyst thin film support. Titanium salts, such as a titanium alkoxide which is a titanium oxide precursor, organic-acid titanium, and a titanium chloride, etc. are applied as an approach of giving titanium oxide to base material front faces, such as glass, a metal, ceramics, and various plastics, and there are an approach which can be burned, the approach of applying the mixture of titanium oxide fine particles, a sol, and a binder, etc. When manufacturing such the photocatalyst structure, it was difficult to use a thick film very much for the application which needs transparency in order to nebula-ize the film containing titanium oxide if the one where a titanium oxide thin film is thicker thickens thickness although effectiveness is high. Then, if the titanium oxide of a particle 50nm or less is used in order to acquire transparency, although it will be easy to form a transparent membrane, if it is going to obtain thickness which exceeds 1 micrometer using titanium oxide 50nm or less, the film will become easy to crocodile at the time of membrane formation. The fall of adhesion to a membranous base material can be caused, and membranous [ some ] cannot make dedropping and the photocatalyst effectiveness a crack not only to have a problem in appearance, but maintain. Although this crack could be prevented by adding the ingredient for easing the contraction stress which caused the crack in coating liquid, or preparing independently the layer which eases stress between coating liquid and a base material, it was inadequate as the fundamental solution approaches — any approach reduces photocatalyst activity or a manufacturing cost increases.

[0003]

[Problem(s) to be Solved by the Invention] Although, as for enlarging the particle diameter of the titanium oxide used as a photocatalyst, it turned out that effectiveness is in crack prevention, it was a big technical problem at an antinomy to have linked increase of particle diameter directly with the fall of transparency, and to reconcile crack prevention of the film with reservation of high transparency. This invention solves these problems by examining the physical properties and the amount of alcohol of titanium oxide.

[0004]

[Means for Solving the Problem] That is, it is related with the titanium oxide content photocatalyst coating liquid characterized by for this invention containing the titanium oxide (TiO<sub>2</sub>) whose mean particle diameter is 50nm – 120nm and crystal particle diameter of 6–18nm, and containing an alcoholic solvent for a silica compound (SiO<sub>2</sub>) 60% of the weight or more 0.1 to 10% of the weight 0.1 to 10% of the weight in the coating liquid which makes the thin film which uses titanium oxide as a principal component form on a base material, and its manufacture approach. Furthermore, this invention relates to the titanium oxide transparency thin film support photocatalyst structure which has the high catalytic activity which used the coating liquid concerned, and practical film reinforcement again.

[0005]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. the titanium oxide used in this invention — a particle with a mean particle diameter of 50nm – 120nm — it is a 70nm – 100nm particle more preferably. Mean particle diameter can be measured by the scattering-about method using laser. It is difficult for the transparency of a paint film to make thickness increase [ mean particle diameter ] by the less than 50nm particle, since it becomes easy to crocodile at the time of membrane formation, although mean particle diameter becomes high. On the other hand, when mean particle diameter is larger than 120nm, since titanium oxide is white pigments, originally, concealment nature is high and nebula-izes a paint film. Moreover, depending on a coating liquid presentation, precipitate may be generated during storage.

[0006] Although the titanium oxide of this invention uses anatase mold titanium oxide as a principal component, some rutile type titanium dioxide may be intermingled. By the way, in the coating liquid of this invention, it is [ 6nm – 18nm of diameters of microcrystal ] required to contain 8nm – 12nm titanium oxide 0.1 to 10% of the weight still more preferably. That is, less than 6nm of the diameter of microcrystal may not only be enough as the photocatalyst effectiveness, but such a microcrystal causes a membranous crack. Moreover, if it exceeds 18nm, in connection with it, the mean particle diameter of titanium oxide will also become large, if it is made a thick film, it will nebula-ize, and it cannot be adapted for the application which needs transparency.

[0007] By the way, although the titanium oxide which has such mean particle diameter and a diameter of microcrystal may introduce this by what kind of approach in case it manufactures coating liquid, to distribute to homogeneity is required, without causing precipitate and condensation in coating liquid.

[0008] Since it is difficult, as for distributing the titanium oxide of fine particles to homogeneity in coating liquid, it is desirable to introduce by the approach of a titanium oxide sol preferably. Although especially the manufacture approach of a titanium oxide sol is not limited, the manufacture approach which can control mean particle diameter and the diameter of microcrystal freely is

desirable.

[0009] As the manufacture approach of such titanium oxide, amalgam decomposition of the powdered anatase mold titanium oxide may be carried out under existence of an acid and alkali, and particle diameter may be controlled by grinding. Moreover, control of the diameter of microcrystal and particle diameter may be performed [ sulfuric-acid titanium or a titanium chloride ] for a pyrolysis or the water titanium oxide obtained by carrying out neutralization decomposition by the physical and chemical approach. A distributed stabilizer may be used in order to give the distributed stability in the inside of a sol solution.

[0010] Although various kinds of distributed stabilizers can be used especially as a distributed stabilizer, without being limited, an acid or alkaline distributed stabilizer is used preferably. As an acid distributed stabilizer, organic acids, such as mineral acids, such as a nitric acid and a hydrochloric acid, a carboxylic acid, hydroxy acid, and polycarboxylic acid, etc. are mentioned. The alkanolamines which added the hydroxy group to a carboxylic acid, the alkali-metal salt of polycarboxylic acid and ammonia, the amines of the 1-4th class, and them as an alkaline distributed stabilizer are mentioned as a good example. these distribution stabilizer is independent — or it can be used together and used. An acid and alkaline dispersant can also be used for coincidence. When an organic acid is used as a distributed stabilizer, especially since it is hard to corrode the facility which pH does not fall extremely in addition to a miscibility with the organic solvent mentioned later being good, and is used at the time of manufacture, it is desirable. Especially as a class of organic acid, an acetic acid, oxalic acid, a glycolic acid, a lactic acid, a tartaric acid, a malic acid, a citric acid, etc. are desirable. It is desirable that it is in coating liquid at 0.005 – 5 % of the weight, and although the amount of an organic acid may make this contain at the time of titanium oxide sol manufacture and may add a part at the time of coating liquid preparation, its mode of the whole company is desirable generally. Titanium oxide condenses that it is less than 0.005 % of the weight, and it becomes easy to sediment, and if [ than 5 % of the weight ] more, in a paint film, an organic acid will remain and the adhesion of a paint film and transparency will be checked. Moreover, even if it uses an organic acid, pH of coating liquid should be adjusted to two or more. When pH becomes two or less, there is a possibility of making a metal corroding.

[0011] Now, the concentration in the coating liquid of said titanium oxide used in this invention is prepared so that it may be 0.1 – 10 % of the weight as  $TiO_2$ . In 1-time coating, the thickness of a paint film is thin in the concentration in coating liquid being less than 0.1 % of the weight, and two coats is required and is not economical. On the other hand, since the viscosity of coating liquid becomes high and handling nature worsens when exceeding 10 % of the weight, it is not desirable. 1 – 5 % of the weight is chosen more preferably.

[0012] As a silica compound of this invention, the condensate of alkoxysilane or alkoxy silane, hydrolyzate, a silicone varnish, etc. can be used. Although the alkoxysilane of three organic functions is generally called a silane coupling agent in many cases, it calls alkoxysilane the compound which one or more alkoxy groups have combined with silicon 1 molecule in this invention. When it illustrates concretely, as 4 organic-functions alkoxysilane A tetramethoxy silane, As a tetra-ethoxy silane, tetra-propoxysilane, and alkoxysilane of three organic functions, methyl trimethoxysilane, Methyl triethoxysilane, phenyl trimethoxysilane, phenyl triethoxysilane, Vinyltrimethoxysilane, vinyltriethoxysilane, methacryloxy propyl trimethoxysilane, Glycide propoxy trimethoxysilane, GURISHIRO propylmethyl diethoxysilane, Aminopropyl triethoxysilane, N-aminoethyl aminopropyl trimethoxysilane, As mercapto propyltrimethoxysilane and alkoxy silane of two organic functions, there are dimethyl dimethoxysilane, dimethyl diethoxysilane, diphenyl dimethoxysilane, diphenyl diethoxysilane, etc. As a condensate, the condensate of 4 organic-functions alkoxysilane of silicate 40, silicate 48, and silicate 51 grade mentions, and it is \*\*\*\*\*.

[0013] Moreover, the thing which made alkoxysilane hydrolyze as hydrolyzate using an organic solvent, water, and a catalyst can be used. Among these silica compounds, especially the alcoholic silica sol that are a tetramethoxy silane, a tetra-ethoxy silane, silicate 40, silicate 48, silicate 51, and those hydrolysis products can fix the film on a base material firmly, and is suitable especially from a comparatively cheap thing.

[0014] Especially the manufacture approach of the above-mentioned alcoholic silica sol is not limited, may perform the hydrolysis reaction of alkoxysilane in coating liquid, and partial hydrolysis may be carried out and it may add hydrolysis or the thing which already became an alcoholic silica sol for alkoxysilane in titanium oxide liquid. The paint film which was excellent in adhesion can be formed by including a silica compound one to 5% of the weight more preferably 0.1 to 10% of the weight as  $SiO_2$  in coating liquid in this invention. At less than 0.1 % of the weight, the adhesion of a paint film gets worse extremely and a silica compound content is not desirable. Moreover, at 10 % of the weight or more, it becomes high, and handling nature not only worsens, but the viscosity of coating liquid may gel under the effect of temperature, while coating liquid keeps it.

[0015] Although these silica compounds are mixed with titanium oxide and it is prepared by coating liquid, even if it satisfies the above-mentioned conditions only to both adjustment, the purpose of this invention cannot be attained. In order to make the purpose of this invention attain, it is using an alcoholic solvent in addition to the above-mentioned conditions. Cellosolve which is polyhydric alcohol and those ester, such as monovalence lower alcohol, such as a methanol, ethanol, propanol, and a butanol, ethylene glycol, and propylene glycol, as an alcoholic solvent to be used is mentioned as a good example. The amount of a solvent alcoholic [ these ] is 60 % of the weight or more among coating liquid. At less than 60 % of the weight, it has high transparency and a thick paint film without a crack cannot be obtained.

[0016] Although not limited especially about the manufacture approach of the coating liquid of this invention, it can manufacture easily by mixing the above-mentioned titanium oxide, a silicon compound, and an alcoholic solvent at a predetermined rate, for example. It agitates until mixed sequence is also arbitrary, and is good and all components are mixed by homogeneity. Just before creating the photocatalyst structure (i.e., just before adjustment of coating liquid applies this invention coating liquid to various base materials), and it may be kept as coating liquid and it may be set. [ adjustment ] When there is the need of adjusting pH on account of the facility which creates the photocatalyst structure etc., it can also adjust to pH of a request just before the time of coating liquid manufacture, or spreading with an acid or alkali. To pH adjustment of the coating liquid of this invention, an above-mentioned organic acid and amines are especially desirable, and it is adjusted to any value in the range of pH 2-12. Since a facility may be made to corrode by two or less pH, it is not desirable. Moreover, since titanium oxide and a silica compound precipitate by 12 or more pH or coating liquid thickens extremely, it is not desirable. When using a titanium oxide sol, pH can also be adjusted in advance at the time of adjustment of a titanium oxide sol.

[0017] This invention coating liquid can be applied to plastics, such as metals, such as ceramics, such as a tile, and a tile, glass, iron, and aluminum, an acrylic, PET, a polycarbonate, and vinyl chloride, various kinds of paint front faces, concrete and a mortar front face, cloth, paper, etc., and can be made into the photocatalyst structure.

[0018] As for either, the shape of tabular and a film, a molding object, etc. are possible for a base material configuration. As an approach of applying coating liquid on a base material and making a titanium oxide thin film forming, various kinds of methods of application, such as brush coating, a spray coating cloth, a spin coat, a DIP coat, a roll coat, a gravure coat, and a bar coat, can be

chosen in consideration of the configuration of a base material. Although desiccation of coating liquid changes with classes of base material, it usually heat-treats below 300 degrees C. When using glass and ceramics as a base material, adhesion [ as opposed to the base material of a paint film in the direction processed at high temperature ] becomes good. However, above 600 degrees C, the fall of the specific surface area by sintering of titanium oxide is remarkable, and the catalyst effectiveness falls. Moreover, as for heat treatment temperature, in the case of plastics, such as an acrylic, PET, a polycarbonate, and a vinyl chloride, a base material becomes 150 degrees C or less from the thermal resistance of a base material. The catalyst effectiveness becomes high so that the thickness of a titanium oxide thin film is thick, but since an increment and the catalyst effectiveness of thickness stop being necessarily proportional when set to 5 micrometers or more, generally the thickness beyond this is not economical. Moreover, since there is possibility of a crack when thickness is too thick, it is about 0.2-5 micrometers practical.

[0019] When using a plastics metallurgy group as a base material in paint film formation, in order to raise further further the adhesion of a base material and a titanium oxide thin film, a glue line can be prepared between a base material and a titanium oxide thin film. What what has high compatibility is desirable to both a base material and a titanium oxide thin film presentation, and contains acrylic resin and silicon in it as a glue line at coincidence can form the tough high glue line of adhesion, especially discovers the effectiveness excellent in crack prevention of the photocatalyst layer formed with this invention coating liquid, and is suitable. A glue line can be made to form easily by applying the coating constituent containing the above-mentioned component by the same approach as this invention coating liquid. Although the thickness of a glue line is not limited, sufficient adhesion can be given if it is about 0.2 micrometers or more. What contains acrylic resin and silicon in coincidence as a coating constituent which forms the glue line in this invention as above-mentioned is desirable, the silicone content in a coating constituent is SiO<sub>2</sub> conversion, and it is desirable that it is 5 - 50 % of the weight to the total amount of desiccation solid content. This range crocodiles with the highest adhesion force, and the prevention effectiveness is demonstrated. The measuring method of this silicone content (SiO<sub>2</sub>) is measured according to the measuring method of the ash content in the heating residue of a publication to JIS K 5400-8.

[0020] The coating constituent of the above-mentioned glue line formation can be easily manufactured by mixing organic silicon compounds, such as for example, a silica sol, and silicone resin, alkoxysilane, in an acrylic resin solution. Moreover, the acrylic denaturation silicon resin and silicon denaturation acrylic resin which change to acrylic resin or contain silicon in acrylic intramolecular by covalent bond with acrylic resin can also be used. Although toluene, a xylene, a ketone, alcohol, etc. are mentioned as a solvent of coating constituent manufacture, the emulsion type of a drainage system may be used. The titanium oxide content photocatalyst coating liquid of this invention can make the photocatalyst paint film of high performance without the crack which has high transparency form, since it is constituted as a full account was given above, when this is applied to various base materials.

[0021]

[Example] This invention is not limited by those examples, although an example is given to below and the detail of invention described so far is concretely explained to it. Moreover, unless it refuses especially, all %s show weight %.

[0022] (Example 1) After diluting TiO<sub>2</sub> 26% of titanium oxide sol A-6 by Taki Chemical Co., Ltd. with ion exchange water until the titanium oxide (TiO<sub>2</sub>) content became 3.5%, 5h hydrothermal processing was carried out at 140 degrees C. After adding citric-acid 1 hydrate until it was set to pH3.0 in this sol liquid, ultrafiltration membrane was used and condensed [ washed and ] and the opalescence sol (A) of pH3.3 which contains 1.5% of citric acids for titanium oxide with 10.2nm [ of diameters of microcrystal ] and a mean particle diameter of 82nm 15% was obtained. Addition mixing of the ethanol 616 section and the tetramethoxy silane (2= 39.5% of SiO(s)) 51 made from KISHIDA Chemistry section was carried out at the this (sol A) 333 section, and this invention photocatalyst coating liquid of 5% of titanium oxide contents, 2% of silica compound (SiO<sub>2</sub>) contents, the 62% of the amounts of alcoholic solvents, and 0.5% of citric-acid contents was obtained. pH of this coating liquid was 4.2, viscosity was 3.6 mPa-s, and it was the colloidal solution of opalescence. Spin coating of this liquid was carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and this invention photocatalyst structure was obtained. This photocatalyst film was transparent and the rate of haze of the film measured by COH [ by Nippon Denshoku Industries Co., Ltd. ]-300A was 0.7%.

[0023] (Example 2) The gamma-meta-acryloxypropyltrimethoxysilane 10 section, the methacrylic-acid 2-hydroxyethyl 5 section, the methyl-methacrylate 17.5 section, the acrylic-acid n-butyl 10 section, the styrene 7.5 section, the xylene 47 section, and the t-butylperoxy-2-ethylhexanoate 3 section were put into 5L reaction containers, and the polymerization was carried out to them with the conventional method. The obtained resin 100 weight section, the MKS methyl silicate MS-56 (Mitsubishi Chemical tetramethyl silicate partial hydrolysate condensate, average value of n = 10) 50 weight section, the dibutyltin laurate 1 weight section, the xylene 700 weight section, and the isopropyl alcohol 150 weight section were put into 5another L reaction containers, it mixed and agitated and the glue line coating constituent was prepared. The silicone content in this coating constituent was 38% (SiO<sub>2</sub>) to the total amount of desiccation solid content. Spin coating of this coating constituent for glue lines was carried out so that dry weight might become the acrylic board of 2 with 10mg 40cm, spin coating of this invention photocatalyst coating liquid further obtained in the example 1 was carried out so that dry weight might be set to about 6mg (0.5 micrometers in thickness), and this invention photocatalyst structure was obtained. This photocatalyst film was transparent and the rate of haze of the film measured by COH [ by Nippon Denshoku Industries Co., Ltd. ]-300A was 0.7%.

[0024] (Example 3) Spin coating of the coating coating constituent for glue lines obtained in the example 2 was carried out so that dry weight might become the acrylic board of 2 with 10mg 40cm, spin coating of this invention photocatalyst coating liquid further obtained in the example 1 was carried out so that dry weight might be set to about 12mg (1.0 micrometers in thickness), and this invention photocatalyst structure was obtained. This photocatalyst film was transparent and the rate of haze was 1.0%.

[0025] (Example 4) The ammonia of the mole ratio 0.5 to titanium oxide (TiO<sub>2</sub>) was added to the titanium oxide sol A-6 by Taki Chemical Co., Ltd. as an aqueous ammonia solution, ion exchange water was added further, and the titanium oxide (TiO<sub>2</sub>) content was adjusted to 3.5%. 5h hydrothermal processing of this liquid was carried out at 145 degrees C. After, carrying out 3h hydrothermal processing at 120 more degrees C in addition until the malic acid was set to pH2.6 in this liquid, ultrafiltration membrane was used and condensed [ washed and ], adding a malic acid, and the opalescence sol of pH3.0 which contains a malic acid for titanium oxide with 14.8nm [ of diameters of microcrystal ] and a mean particle diameter of 93nm 0.7% 10% was obtained. The ethyl silicate 40 (2= 40% of SiO(s)) 16 made from Tama Chemical industry section, the methanol 50 section, the ethanol 650 section, ion exchange water 33, and the oxalic acid 2 hydrate 1 section were mixed in this sol 250 section, and this invention photocatalyst coating liquid of 2.5% of titanium oxide contents, 0.64 % of the weight of silica compound (SiO<sub>2</sub>) contents, the 70% of the amounts of alcoholic solvents, and 0.2% of organic-acid contents was obtained. pH of this coating liquid was 3.8, viscosity was

3.1 mPa-s, and it was the white colloidal solution. Spin coating of this liquid was carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and this invention photocatalyst structure was obtained. The rate of haze which this photocatalyst film is a transparent membrane accompanied by the interference color, and was measured by COH[ by Nippon Denshoku Industries Co., Ltd. ]-300A was 1.1%.

[0026] (Example 5) Spin coating of the coating constituent for glue lines obtained in the example 2 was carried out so that dry weight might become the acrylic board of 2 with 10mg 40cm, spin coating of the photocatalyst coating liquid further obtained in the example 1 was carried out so that dry weight might be set to about 6mg (0.5 micrometers in thickness), and this invention photocatalyst structure was obtained. This photocatalyst film was transparent and the rate of haze was 1.1%. These two acrylic boards were put into the separable flask of 1.9L \*\*, the acetaldehyde was introduced so that it might become the concentration of 100 ppm, and when the black light was irradiated for 90 minutes so that it might become the ultraviolet-rays reinforcement of 1 mW/cm<sup>2</sup> on a film front face, the acetaldehyde concentration in a container was falling to 26 ppm.

[0027] (Example 6) Spin coating of the coating constituent for glue lines obtained in the example 2 was carried out so that dry weight might become the acrylic board of 2 with 10mg 40cm, spin coating of the photocatalyst coating liquid further obtained in the example 1 was carried out so that dry weight might be set to about 12mg (1.0 micrometers in thickness), and this invention photocatalyst structure was obtained. This photocatalyst film was transparent and the rate of haze was 1.5%. These two acrylic boards were put into the separable flask of 1.9L \*\*, the acetaldehyde was introduced so that it might become the concentration of 100 ppm, and when the black light was irradiated for 90 minutes so that it might become the ultraviolet-rays reinforcement of 1 mW/cm<sup>2</sup> on a film front face, the acetaldehyde concentration in a container was falling to 8 ppm.

[0028] (Example 7) After adding 2-aminoethanol to the titanium oxide sol (A) manufactured in the example 1 and adjusting to pH11, it was washed by ultrafiltration membrane again and the opalescence sol (B) of 15% of titanium oxide (TiO<sub>2</sub>) concentration and pH9.3 was obtained. The diameter of microcrystal of the titanium oxide of this sol (B) was 10.2nm, and mean particle diameter was 75nm. It replaced with the sol (A) and this invention photocatalyst coating liquid of opalescence was prepared by the same approach as an example 1 using the sol (B). Spin coating of this liquid was carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and this invention photocatalyst structure was obtained. The rate of haze which this photocatalyst film is a transparent membrane accompanied by the interference color, and was measured by COH[ by Nippon Denshoku Industries Co., Ltd. ]-300A was 0.8%.

[0029] (Example 1 of a comparison) After diluting TiO<sub>2</sub>26% of titanium oxide sol M-6 by Taki Chemical Co., Ltd. with ion exchange water and adjusting it to pH2.5 by the citric acid until the titanium oxide (TiO<sub>2</sub>) content became 4.0%, 3h hydrothermal processing was carried out at 140 degrees C. After washing the obtained sol liquid using ultrafiltration membrane, heating concentration was carried out and the light yellow sol (C) of pH3.3 which contains titanium oxide with 5.0nm [ of diameters of microcrystal ] and a mean particle diameter of 8nm 2.5% of organic acids 15% was obtained. The ethanol 616 section and the tetramethoxy silane (2= 39.5% of SiO(s)) 51 made from KISHIDA Chemistry section were mixed in the this (sol C) 333 section, and photocatalyst coating liquid of 5% of titanium oxide (TiO<sub>2</sub>) contents, 2% of silica compound (SiO<sub>2</sub>) contents, the 62% of the amounts of alcoholic solvents, and 0.8% of organic-acid contents was obtained. pH of this coating liquid was 4.5, viscosity was 5.0 mPa-s, and it was the colloidal solution of light yellow. Although spin coating of this liquid tended to be carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and it was going to create the photocatalyst structure, membranes were not able to be cracked and formed at the time of desiccation.

[0030] (Example 2 of a comparison) After mixing the Taki Chemical Co., Ltd. titanium oxide powder (A-100) (2= 86% of TiO(s)) 100 section, the malic-acid 16 made from Kanto Chemistry section, and the ion-exchange-water 228 section, the bead mill ground and the white sol (D) of pH2.3 which contains titanium oxide with 6nm [ of diameters of microcrystal ] and a mean particle diameter of 400nm 25% was obtained. The ethanol 616 section, the tetramethoxy silane (2= 39.5% of SiO(s)) 51 made from KISHIDA Chemistry section, and the ion-exchange-water 133 section were mixed in the this (sol D) 200 section, and photocatalyst coating liquid of 5% of titanium oxide (TiO<sub>2</sub>) contents, 2% of silica compound (SiO<sub>2</sub>) contents, and the 62% of the amounts of alcoholic solvents was obtained. pH of this coating liquid was 3.9, viscosity was 3.3 mPa-s, and it was the white colloidal solution. Spin coating of this liquid was carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and the photocatalyst structure was obtained. This photocatalyst film was film which became muddy a little, and the rate of haze measured by COH[ by Nippon Denshoku Industries Co., Ltd. ]-300A was 2.8%.

[0031] (Example 3 of a comparison) After diluting TiO<sub>2</sub>26% of titanium oxide sol A-6 by Taki Chemical Co., Ltd. with ion exchange water until the titanium oxide content became 4.0%, 5h hydrothermal processing was carried out at 130 degrees C. After adding a citric acid until it was set to pH3.0 in this sol liquid, ultrafiltration membrane was used and condensed [ washed and ] and the opalescence sol of pH3.3 which contains titanium oxide with 9.2nm [ of diameters of microcrystal ] and a mean particle diameter of 52nm 15% was obtained. The ethanol 300 section, the tetramethoxy silane (2= 39.5% of SiO(s)) 51 made from KISHIDA Chemistry section, and the ion-exchange-water 316 section were mixed in this sol 333 section, and photocatalyst coating liquid of 5% of titanium oxide (TiO<sub>2</sub>) contents, 2% of silica compound (SiO<sub>2</sub>) contents, the 30% of the amounts of alcoholic solvents, and 0.5% of organic-acid contents was obtained. pH of this coating liquid was 4.0, viscosity was 3.0 mPa-s, and it was the colloidal solution of opalescence. Spin coating of this liquid was carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and the photocatalyst structure was obtained. The crack occurred in the membranous periphery and the film exfoliated.

[0032]

[Effect of the Invention] Even if this invention enlarges the particle diameter of the titanium oxide used as a photocatalyst, they are the titanium oxide content photocatalyst coating liquid with which effectiveness is in crack prevention and high transparency was secured, and its manufacture approach.

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TECHNICAL FIELD

[Field of the Invention] About the titanium oxide photocatalyst structure which used the coating liquid concerned for the titanium oxide content photocatalyst coating liquid which uses the photocatalyst effectiveness of titanium oxide and is used for harmful matter removal of NOX etc., deodorization, antifouling, antibacterial, etc., and its manufacture approach list, even if this invention has few cracks of the film at the time of spreading and they use it as a thick film especially, it relates to the titanium oxide content photocatalyst coating liquid which gives the film with high transparency, and its manufacture approach.

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PRIOR ART

[Description of the Prior Art] The titanium oxide photocatalyst is known for effectiveness, such as harmful matter removal of NOX etc., deodorization, antifouling, and antibacterial, being shown by the chemical reaction which absorbs and starts ultraviolet rays. By the way, in order to make the photocatalyst effectiveness discover industrially, it is required on a base material to make a photocatalyst thin film support. Titanium salts, such as a titanium alkoxide which is a titanium oxide precursor, organic-acid titanium, and a titanium chloride, etc. are applied as an approach of giving titanium oxide to base material front faces, such as glass, a metal, ceramics, and various plastics, and there are an approach which can be burned, the approach of applying the mixture of titanium oxide fine particles, a sol, and a binder, etc. When manufacturing such the photocatalyst structure, it was difficult to use a thick film very much for the application which needs transparency in order to nebula-ize the film containing titanium oxide if the one where a titanium oxide thin film is thicker thickens thickness although effectiveness is high. Then, if the titanium oxide of a particle 50nm or less is used in order to acquire transparency, although it will be easy to form a transparent membrane, if it is going to obtain thickness which exceeds 1 micrometer using titanium oxide 50nm or less, the film will become easy to crocodile at the time of membrane formation. The fall of adhesion to a membranous base material can be caused, and membranous [ some ] cannot make dedropping and the photocatalyst effectiveness a crack not only to have a problem in appearance, but maintain. Although this crack could be prevented by adding the ingredient for easing the contraction stress which caused the crack in coating liquid, or preparing independently the layer which eases stress between coating liquid and a base material, it was inadequate as the fundamental solution approaches -- any approach reduces photocatalyst activity or a manufacturing cost increases.

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EFFECT OF THE INVENTION

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[Effect of the Invention] Even if this invention enlarges the particle diameter of the titanium oxide used as a photocatalyst, they are the titanium oxide content photocatalyst coating liquid with which effectiveness is in crack prevention and high transparency was secured, and its manufacture approach.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] Although, as for enlarging the particle diameter of the titanium oxide used as a photocatalyst, it turned out that effectiveness is in crack prevention, it was a big technical problem at an antinomy to have linked increase of particle diameter directly with the fall of transparency, and to reconcile crack prevention of the film with reservation of high transparency. This invention solves these problems by examining the physical properties and the amount of alcohol of titanium oxide.

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## MEANS

[Means for Solving the Problem] That is, it is related with the titanium oxide content photocatalyst coating liquid characterized by for this invention containing the titanium oxide (TiO<sub>2</sub>) whose mean particle diameter is 50nm - 120nm and crystal particle diameter of 6-18nm, and containing an alcoholic solvent for a silica compound (SiO<sub>2</sub>) 60% of the weight or more 0.1 to 10% of the weight 0.1 to 10% of the weight in the coating liquid which makes the thin film which uses titanium oxide as a principal component form on a base material, and its manufacture approach. Furthermore, this invention relates to the titanium oxide transparency thin film support photocatalyst structure which has the high catalytic activity which used the coating liquid concerned, and practical film reinforcement again.

[0005]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. the titanium oxide used in this invention — a particle with a mean particle diameter of 50nm - 120nm — it is a 70nm - 100nm particle more preferably. Mean particle diameter can be measured by the scattering-about method using laser. It is difficult for the transparency of a paint film to make thickness increase [ mean particle diameter ] by the less than 50nm particle, since it becomes easy to crocodile at the time of membrane formation, although mean particle diameter becomes high. On the other hand, when mean particle diameter is larger than 120nm, since titanium oxide is white pigments, originally, concealment nature is high and nebula-izes a paint film. Moreover, depending on a coating liquid presentation, precipitate may be generated during storage.

[0006] Although the titanium oxide of this invention uses anatase mold titanium oxide as a principal component, some rutile type titanium dioxide may be intermingled. By the way, in the coating liquid of this invention, it is [ 6nm - 18nm of diameters of microcrystal ] required to contain 8nm - 12nm titanium oxide 0.1 to 10% of the weight still more preferably. That is, less than 6nm of the diameter of microcrystal may not only be enough as the photocatalyst effectiveness, but such a microcrystal causes a membranous crack. Moreover, if it exceeds 18nm, in connection with it, the mean particle diameter of titanium oxide will also become large, if it is made a thick film, it will nebula-ize, and it cannot be adapted for the application which needs transparency.

[0007] By the way, although the titanium oxide which has such mean particle diameter and a diameter of microcrystal may introduce this by what kind of approach in case it manufactures coating liquid, to distribute to homogeneity is required, without causing precipitate and condensation in coating liquid.

[0008] Since it is difficult, as for distributing the titanium oxide of fine particles to homogeneity in coating liquid, it is desirable to introduce by the approach of a titanium oxide sol preferably. Although especially the manufacture approach of a titanium oxide sol is not limited, the manufacture approach which can control mean particle diameter and the diameter of microcrystal freely is desirable.

[0009] As the manufacture approach of such titanium oxide, amalgam decomposition of the powdered anatase mold titanium oxide may be carried out under existence of an acid and alkali, and particle diameter may be controlled by grinding. Moreover, control of the diameter of microcrystal and particle diameter may be performed [ sulfuric-acid titanium or a titanium chloride ] for a pyrolysis or the water titanium oxide obtained by carrying out neutralization decomposition by the physical and chemical approach. A distributed stabilizer may be used in order to give the distributed stability in the inside of a sol solution.

[0010] Although various kinds of distributed stabilizers can be used especially as a distributed stabilizer, without being limited, an acid or alkaline distributed stabilizer is used preferably. As an acid distributed stabilizer, organic acids, such as mineral acids, such as a nitric acid and a hydrochloric acid, a carboxylic acid, hydroxy acid, and polycarboxylic acid, etc. are mentioned. The alkanolamines which added the hydroxy group to a carboxylic acid, the alkali-metal salt of polycarboxylic acid and ammonia, the amines of the 1-4th class, and them as an alkaline distributed stabilizer are mentioned as a good example. these distribution stabilizer is independent — or it can be used together and used. An acid and alkaline dispersant can also be used for coincidence. When an organic acid is used as a distributed stabilizer, especially since it is hard to corrode the facility which pH does not fall extremely in addition to a miscibility with the organic solvent mentioned later being good, and is used at the time of manufacture, it is desirable. Especially as a class of organic acid, an acetic acid, oxalic acid, a glycolic acid, a lactic acid, a tartaric acid, a malic acid, a citric acid, etc. are desirable. It is desirable that it is in coating liquid at 0.005 - 5 % of the weight, and although the amount of an organic acid may make this contain at the time of titanium oxide sol manufacture and may add a part at the time of coating liquid preparation, its mode of the whole company is desirable generally. Titanium oxide condenses that it is less than 0.005 % of the weight, and it becomes easy to sediment, and if [ than 5 % of the weight ] more, in a paint film, an organic acid will remain and the adhesion of a paint film and transparency will be checked. Moreover, even if it uses an organic acid, pH of coating liquid should be adjusted to two or more. When pH becomes two or less, there is a possibility of making a metal corroding.

[0011] Now, the concentration in the coating liquid of said titanium oxide used in this invention is prepared so that it may be 0.1 - 10 % of the weight as TiO<sub>2</sub>. In 1-time coating, the thickness of a paint film is thin in the concentration in coating liquid being less than 0.1 % of the weight, and two coats is required and is not economical. On the other hand, since the viscosity of coating liquid becomes high and handling nature worsens when exceeding 10 % of the weight, it is not desirable. 1 - 5 % of the weight is chosen more preferably.

[0012] As a silica compound of this invention, the condensate of alkoxysilane or alkoxy silane, hydrolyzate, a silicone varnish, etc. can be used. Although the alkoxy silane of three organic functions is generally called a silane coupling agent in many cases, it calls alkoxy silane the compound which one or more alkoxy groups have combined with silicon 1 molecule in this invention. When it illustrates concretely, as 4 organic-functions alkoxy silane A tetramethoxy silane, As a tetra-ethoxy silane, tetra-propoxysilane, and alkoxy silane of three organic functions, methyl trimethoxysilane, Methyl triethoxysilane, phenyl trimethoxysilane, phenyl

triethoxysilane, Vinyltrimethoxysilane, vinyltriethoxysilane, methacryloxy propyl trimethoxysilane, Glycide propoxy trimethoxysilane, GURISHIRO propylmethyl diethoxysilane, Aminopropyl triethoxysilane, N-aminoethyl aminopropyl trimethoxysilane, As mercapto propyltrimethoxysilane and alkoxy silane of two organic functions, there are dimethyl dimethoxysilane, dimethyl diethoxysilane, diphenyl dimethoxysilane, diphenyl diethoxysilane, etc. As a condensate, the condensate of 4 organic-functions alkoxy silane of silicate 40, silicate 48, and silicate 51 grade mentions, and it is \*\*\*\*\*.

[0013] Moreover, the thing which made alkoxy silane hydrolyze as hydrolyzate using an organic solvent, water, and a catalyst can be used. Among these silica compounds, especially the alcoholic silica sol that are a tetramethoxy silane, a tetra-ethoxy silane, silicate 40, silicate 48, silicate 51, and those hydrolysis products can fix the film on a base material firmly, and is suitable especially from a comparatively cheap thing.

[0014] Especially the manufacture approach of the above-mentioned alcoholic silica sol is not limited, may perform the hydrolysis reaction of alkoxy silane in coating liquid, and partial hydrolysis may be carried out and it may add hydrolysis or the thing which already became an alcoholic silica sol for alkoxy silane in titanium oxide liquid. The paint film which was excellent in adhesion can be formed by including a silica compound one to 5% of the weight more preferably 0.1 to 10% of the weight as SiO<sub>2</sub> in coating liquid in this invention. At less than 0.1 % of the weight, the adhesion of a paint film gets worse extremely and a silica compound content is not desirable. Moreover, at 10 % of the weight or more, it becomes high, and handling nature not only worsens, but the viscosity of coating liquid may gel under the effect of temperature, while coating liquid keeps it.

[0015] Although these silica compounds are mixed with titanium oxide and it is prepared by coating liquid, even if it satisfies the above-mentioned conditions only to both adjustment, the purpose of this invention cannot be attained. In order to make the purpose of this invention attain, it is using an alcoholic solvent in addition to the above-mentioned conditions. Cellosolve which is polyhydric alcohol and those ester, such as monovalence lower alcohol, such as a methanol, ethanol, propanol, and a butanol, ethylene glycol, and propylene glycol, as an alcoholic solvent to be used is mentioned as a good example. The amount of a solvent alcoholic [ these ] is 60 % of the weight or more among coating liquid. At less than 60 % of the weight, it has high transparency and a thick paint film without a crack cannot be obtained.

[0016] Although not limited especially about the manufacture approach of the coating liquid of this invention, it can manufacture easily by mixing the above-mentioned titanium oxide, a silicon compound, and an alcoholic solvent at a predetermined rate, for example. It agitates until mixed sequence is also arbitrary, and is good and all components are mixed by homogeneity. Just before creating the photocatalyst structure (i.e., just before adjustment of coating liquid applies this invention coating liquid to various base materials), and it may be kept as coating liquid and it may be set. [ adjustment ] When there is the need of adjusting pH on account of the facility which creates the photocatalyst structure etc., it can also adjust to pH of a request just before the time of coating liquid manufacture, or spreading with an acid or alkali. To pH adjustment of the coating liquid of this invention, an above-mentioned organic acid and amines are especially desirable, and it is adjusted to any value in the range of pH 2-12. Since a facility may be made to corrode by two or less pH, it is not desirable. Moreover, since titanium oxide and a silica compound precipitate by 12 or more pH or coating liquid thickens extremely, it is not desirable. When using a titanium oxide sol, pH can also be adjusted in advance at the time of adjustment of a titanium oxide sol.

[0017] This invention coating liquid can be applied to plastics, such as metals, such as ceramics, such as a tile, and a tile, glass, iron, and aluminum, an acrylic, PET, a polycarbonate, and vinyl chloride, various kinds of paint front faces, concrete and a mortar front face, cloth, paper, etc., and can be made into the photocatalyst structure.

[0018] As for either, the shape of tabular and a film, a molding object, etc. are possible for a base material configuration. As an approach of applying coating liquid on a base material and making a titanium oxide thin film forming, various kinds of methods of application, such as brush coating, a spray coating cloth, a spin coat, a DIP coat, a roll coat, a gravure coat, and a bar coat, can be chosen in consideration of the configuration of a base material. Although desiccation of coating liquid changes with classes of base material, it usually heat-treats below 300 degrees C. When using glass and ceramics as a base material, adhesion [ as opposed to the base material of a paint film in the direction processed at high temperature ] becomes good. However, above 600 degrees C, the fall of the specific surface area by sintering of titanium oxide is remarkable, and the catalyst effectiveness falls. Moreover, as for heat treatment temperature, in the case of plastics, such as an acrylic, PET, a polycarbonate, and a vinyl chloride, a base material becomes 150 degrees C or less from the thermal resistance of a base material. The catalyst effectiveness becomes high so that the thickness of a titanium oxide thin film is thick, but since an increment and the catalyst effectiveness of thickness stop being necessarily proportional when set to 5 micrometers or more, generally the thickness beyond this is not economical. Moreover, since there is possibility of a crack when thickness is too thick, it is about 0.2-5 micrometers practical.

[0019] When using a plastics metallurgy group as a base material in paint film formation, in order to raise further further the adhesion of a base material and a titanium oxide thin film, a glue line can be prepared between a base material and a titanium oxide thin film. What has high compatibility is desirable to both a base material and a titanium oxide thin film presentation, and contains acrylic resin and silicon in it as a glue line at coincidence can form the tough high glue line of adhesion, especially discovers the effectiveness excellent in crack prevention of the photocatalyst layer formed with this invention coating liquid, and is suitable. A glue line can be made to form easily by applying the coating constituent containing the above-mentioned component by the same approach as this invention coating liquid. Although the thickness of a glue line is not limited, sufficient adhesion can be given if it is about 0.2 micrometers or more. What contains acrylic resin and silicon in coincidence as a coating constituent which forms the glue line in this invention as above-mentioned is desirable, the silicone content in a coating constituent is SiO<sub>2</sub> conversion, and it is desirable that it is 5 - 50 % of the weight to the total amount of desiccation solid content. This range crocodiles with the highest adhesion force, and the prevention effectiveness is demonstrated. The measuring method of this silicone content (SiO<sub>2</sub>) is measured according to the measuring method of the ash content in the heating residue of a publication to JIS K 5400-8.

[0020] The coating constituent of the above-mentioned glue line formation can be easily manufactured by mixing organic silicon compounds, such as for example, a silica sol, and silicone resin, alkoxy silane, in an acrylic resin solution. Moreover, the acrylic denaturation silicon resin and silicon denaturation acrylic resin which change to acrylic resin or contain silicon in acrylic intramolecular by covalent bond with acrylic resin can also be used. Although toluene, a xylene, a ketone, alcohol, etc. are mentioned as a solvent of coating constituent manufacture, the emulsion type of a drainage system may be used. The titanium oxide content photocatalyst coating liquid of this invention can make the photocatalyst paint film of high performance without the crack which has high transparency form, since it is constituted as a full account was given above, when this is applied to various base materials.

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## EXAMPLE

[Example] This invention is not limited by those examples, although an example is given to below and the detail of invention described so far is concretely explained to it. Moreover, unless it refuses especially, all %s show weight %.

[0022] (Example 1) After diluting TiO<sub>2</sub> 26% of titanium oxide sol A-6 by Taki Chemical Co., Ltd. with ion exchange water until the titanium oxide (TiO<sub>2</sub>) content became 3.5%, 5h hydrothermal processing was carried out at 140 degrees C. After adding citric-acid 1 hydrate until it was set to pH3.0 in this sol liquid, ultrafiltration membrane was used and condensed [ washed and ] and the opalescence sol (A) of pH3.3 which contains 1.5% of citric acids for titanium oxide with 10.2nm [ of diameters of microcrystal ] and a mean particle diameter of 82nm 15% was obtained. Addition mixing of the ethanol 616 section and the tetramethoxy silane (2= 39.5% of SiO(s)) 51 made from KISHIDA Chemistry section was carried out at the this (sol A) 333 section, and this invention photocatalyst coating liquid of 5% of titanium oxide contents, 2% of silica compound (SiO<sub>2</sub>) contents, the 62% of the amounts of alcoholic solvents, and 0.5% of citric-acid contents was obtained. pH of this coating liquid was 4.2, viscosity was 3.6 mPa-s, and it was the colloidal solution of opalescence. Spin coating of this liquid was carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and this invention photocatalyst structure was obtained. This photocatalyst film was transparent and the rate of haze of the film measured by COH [ by Nippon Denshoku Industries Co., Ltd. ]-300A was 0.7%.

[0023] (Example 2) The gamma-meta-acryloxypropyltrimethoxysilane 10 section, the methacrylic-acid 2-hydroxyethyl 5 section, the methyl-methacrylate 17.5 section, the acrylic-acid n-butyl 10 section, the styrene 7.5 section, the xylene 47 section, and the t-butylperoxy-2-ethylhexanoate 3 section were put into 5L reaction containers, and the polymerization was carried out to them with the conventional method. The obtained resin 100 weight section, the MKS methyl silicate MS-56 (Mitsubishi Chemical tetramethyl silicate partial hydrolysate condensate, average value of n = 10) 50 weight section, the dibutyltin laurate 1 weight section, the xylene 700 weight section, and the isopropyl alcohol 150 weight section were put into 5 another L reaction containers, it mixed and agitated and the glue line coating constituent was prepared. The silicone content in this coating constituent was 38% (SiO<sub>2</sub>) to the total amount of desiccation solid content. Spin coating of this coating constituent for glue lines was carried out so that dry weight might become the acrylic board of 2 with 10mg 40cm, spin coating of this invention photocatalyst coating liquid further obtained in the example 1 was carried out so that dry weight might be set to about 6mg (0.5 micrometers in thickness), and this invention photocatalyst structure was obtained. This photocatalyst film was transparent and the rate of haze of the film measured by COH [ by Nippon Denshoku Industries Co., Ltd. ]-300A was 0.7%.

[0024] (Example 3) Spin coating of the coating constituent for glue lines obtained in the example 2 was carried out so that dry weight might become the acrylic board of 2 with 10mg 40cm, spin coating of this invention photocatalyst coating liquid further obtained in the example 1 was carried out so that dry weight might be set to about 12mg (1.0 micrometers in thickness), and this invention photocatalyst structure was obtained. This photocatalyst film was transparent and the rate of haze was 1.0%.

[0025] (Example 4) The ammonia of the mole ratio 0.5 to titanium oxide (TiO<sub>2</sub>) was added to the titanium oxide sol A-6 by Taki Chemical Co., Ltd. as an aqueous ammonia solution, ion exchange water was added further, and the titanium oxide (TiO<sub>2</sub>) content was adjusted to 3.5%. 5h hydrothermal processing of this liquid was carried out at 145 degrees C. After, carrying out 3h hydrothermal processing at 120 more degrees C in addition until the malic acid was set to pH2.6 in this liquid, ultrafiltration membrane was used and condensed [ washed and ], adding a malic acid, and the opalescence sol of pH3.0 which contains a malic acid for titanium oxide with 14.8nm [ of diameters of microcrystal ] and a mean particle diameter of 93nm 0.7% 10% was obtained. The ethyl silicate 40 (2= 40% of SiO(s)) 16 made from Tama Chemical industry section, the methanol 50 section, the ethanol 650 section, ion exchange water 33, and the oxalic acid 2 hydrate 1 section were mixed in this sol 250 section, and this invention photocatalyst coating liquid of 2.5% of titanium oxide contents, 0.64 % of the weight of silica compound (SiO<sub>2</sub>) contents, the 70% of the amounts of alcoholic solvents, and 0.2% of organic-acid contents was obtained. pH of this coating liquid was 3.8, viscosity was 3.1 mPa-s, and it was the white colloidal solution. Spin coating of this liquid was carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and this invention photocatalyst structure was obtained. The rate of haze which this photocatalyst film is a transparent membrane accompanied by the interference color, and was measured by COH [ by Nippon Denshoku Industries Co., Ltd. ]-300A was 1.1%.

[0026] (Example 5) Spin coating of the coating constituent for glue lines obtained in the example 2 was carried out so that dry weight might become the acrylic board of 2 with 10mg 40cm, spin coating of the photocatalyst coating liquid further obtained in the example 1 was carried out so that dry weight might be set to about 6mg (0.5 micrometers in thickness), and this invention photocatalyst structure was obtained. This photocatalyst film was transparent and the rate of haze was 1.1%. These two acrylic boards were put into the separable flask of 1.9L \*\*, the acetaldehyde was introduced so that it might become the concentration of 100 ppm, and when the black light was irradiated for 90 minutes so that it might become the ultraviolet-rays reinforcement of 1 mW/cm<sup>2</sup> on a film front face, the acetaldehyde concentration in a container was falling to 26 ppm.

[0027] (Example 6) Spin coating of the coating constituent for glue lines obtained in the example 2 was carried out so that dry weight might become the acrylic board of 2 with 10mg 40cm, spin coating of the photocatalyst coating liquid further obtained in the example 1 was carried out so that dry weight might be set to about 12mg (1.0 micrometers in thickness), and this invention photocatalyst structure was obtained. This photocatalyst film was transparent and the rate of haze was 1.5%. These two acrylic boards were put into the separable flask of 1.9L \*\*, the acetaldehyde was introduced so that it might become the concentration of 100 ppm, and when the black light was irradiated for 90 minutes so that it might become the ultraviolet-rays reinforcement of 1 mW/cm<sup>2</sup> on a film front face, the acetaldehyde concentration in a container was falling to 8 ppm.

[0028] (Example 7) After adding 2-aminoethanol to the titanium oxide sol (A) manufactured in the example 1 and adjusting to pH11, it was washed by ultrafiltration membrane again and the opalescence sol (B) of 15% of titanium oxide (TiO<sub>2</sub>) concentration and pH9.3 was obtained. The diameter of microcrystal of the titanium oxide of this sol (B) was 10.2nm, and mean particle diameter was 75nm. It replaced with the sol (A) and this invention photocatalyst coating liquid of opalescence was prepared by the same approach as an example 1 using the sol (B). Spin coating of this liquid was carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and this invention photocatalyst structure was obtained. The rate of haze which this photocatalyst film is a transparent membrane accompanied by the interference color, and was measured by COH[ by Nippon Denshoku Industries Co., Ltd. ]-300A was 0.8%.

[0029] (Example 1 of a comparison) After diluting TiO<sub>2</sub>26% of titanium oxide sol M-6 by Taki Chemical Co., Ltd. with ion exchange water and adjusting it to pH2.5 by the citric acid until the titanium oxide (TiO<sub>2</sub>) content became 4.0%, 3h hydrothermal processing was carried out at 140 degrees C. After washing the obtained sol liquid using ultrafiltration membrane, heating concentration was carried out and the light yellow sol (C) of pH3.3 which contains titanium oxide with 5.0nm [ of diameters of microcrystal ] and a mean particle diameter of 8nm 2.5% of organic acids 15% was obtained. The ethanol 616 section and the tetramethoxy silane (2= 39.5% of SiO(s)) 51 made from KISHIDA Chemistry section were mixed in the this (sol C) 333 section, and photocatalyst coating liquid of 5% of titanium oxide (TiO<sub>2</sub>) contents, 2% of silica compound (SiO<sub>2</sub>) contents, the 62% of the amounts of alcoholic solvents, and 0.8% of organic-acid contents was obtained. pH of this coating liquid was 4.5, viscosity was 5.0 mPa-s, and it was the colloidal solution of light yellow. Although spin coating of this liquid tended to be carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and it was going to create the photocatalyst structure, membranes were not able to be cracked and formed at the time of desiccation.

[0030] (Example 2 of a comparison) After mixing the Taki Chemical Co., Ltd. titanium oxide powder (A-100) (2= 86% of TiO(s)) 100 section, the malic-acid 16 made from Kanto Chemistry section, and the ion-exchange-water 228 section, the bead mill ground and the white sol (D) of pH2.3 which contains titanium oxide with 6nm [ of diameters of microcrystal ] and a mean particle diameter of 400nm 25% was obtained. The ethanol 616 section, the tetramethoxy silane (2= 39.5% of SiO(s)) 51 made from KISHIDA Chemistry section, and the ion-exchange-water 133 section were mixed in the this (sol D) 200 section, and photocatalyst coating liquid of 5% of titanium oxide (TiO<sub>2</sub>) contents, 2% of silica compound (SiO<sub>2</sub>) contents, and the 62% of the amounts of alcoholic solvents was obtained. pH of this coating liquid was 3.9, viscosity was 3.3 mPa-s, and it was the white colloidal solution. Spin coating of this liquid was carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and the photocatalyst structure was obtained. This photocatalyst film was film which became muddy a little, and the rate of haze measured by COH[ by Nippon Denshoku Industries Co., Ltd. ]-300A was 2.8%.

[0031] (Example 3 of a comparison) After diluting TiO<sub>2</sub>26% of titanium oxide sol A-6 by Taki Chemical Co., Ltd. with ion exchange water until the titanium oxide content became 4.0%, 5h hydrothermal processing was carried out at 130 degrees C. After adding a citric acid until it was set to pH3.0 in this sol liquid, ultrafiltration membrane was used and condensed [ washed and ] and the opalescence sol of pH3.3 which contains titanium oxide with 9.2nm [ of diameters of microcrystal ] and a mean particle diameter of 52nm 15% was obtained. The ethanol 300 section, the tetramethoxy silane (2= 39.5% of SiO(s)) 51 made from KISHIDA Chemistry section, and the ion-exchange-water 316 section were mixed in this sol 333 section, and photocatalyst coating liquid of 5% of titanium oxide (TiO<sub>2</sub>) contents, 2% of silica compound (SiO<sub>2</sub>) contents, the 30% of the amounts of alcoholic solvents, and 0.5% of organic-acid contents was obtained. pH of this coating liquid was 4.0, viscosity was 3.0 mPa-s, and it was the colloidal solution of opalescence. Spin coating of this liquid was carried out so that dry weight might become the glass plate of 2 with about 6mg (0.5 micrometers in thickness) 40cm, and the photocatalyst structure was obtained. The crack occurred in the membranous periphery and the film exfoliated.

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(54) 【発明の名称】 酸化チタン含有光触媒塗布液およびその製造方法ならびに酸化チタン光触媒構造体

## (57) 【要約】

【課題】 高い透明性を有し、且つひび割れのない光触媒膜を得ることは困難であったが、本発明はこの両者を満足する光触媒塗布液を提供する。

【解決手段】 基材上に酸化チタンを主成分とする薄膜を形成させる光触媒塗布液において、平均粒子径が50nm～120nm、結晶子径6～18nmの酸化チタン(TiO<sub>2</sub>)を0.1～10重量%、シリカ化合物(SiO<sub>2</sub>)を0.1～10重量%、アルコール溶媒を60重量%以上含むことを特徴とする酸化チタン含有光触媒塗布液。



## 【特許請求の範囲】

【請求項1】 基材上に酸化チタンを主成分とする薄膜を形成させる光触媒塗布液において、平均粒子径が50nm～120nm、結晶粒子径6～18nmの酸化チタン( $\text{TiO}_2$ )を0.1～10重量%、シリカ化合物( $\text{SiO}_2$ )を0.1～10重量%、アルコール溶媒を60重量%以上含むことを特徴とする酸化チタン含有光触媒塗布液。

【請求項2】 前記酸化チタン含有塗布液に於いて、有機酸を0.005～5重量%含み、且つpHが2以上である請求項1記載の酸化チタン含有光触媒塗布液。

【請求項3】 シリカ化合物がアルコキシシランまたはその縮合物、加水分解物である請求項1または2に記載の酸化チタン含有光触媒塗布液。

【請求項4】 基材上に酸化チタンを主成分とする薄膜を形成させる塗布液の製造方法において、平均粒子径が50nm～120nm、結晶粒子径6～18nmの酸化チタンとシリカ化合物とアルコール溶媒を、酸化チタン( $\text{TiO}_2$ )を0.1～10重量%、シリカ化合物( $\text{SiO}_2$ )を0.1～10重量%、アルコール溶媒を60重量%以上となるように混合することを特徴とする酸化チタン含有光触媒塗布液の製造方法。

【請求項5】 酸化チタン含有光触媒塗布液のpHを2～12になるように調製する事を特徴とする請求項4記載の酸化チタン含有光触媒塗布液の製造方法。

【請求項6】 請求項1～3のいずれか1項記載の酸化チタン含有光触媒塗布液を基材に接着層を介して塗布した光触媒構造体。

【請求項7】 前記接着層がアクリル樹脂およびシリコンを含有した接着層である請求項6に記載の光触媒構造体。

【請求項8】 前記接着層中のシリコン含有量が5～50重量%である請求項7に記載の光触媒構造体。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は酸化チタンの光触媒効果を利用し、 $\text{NO}_x$ などの有害物質除去、脱臭、防汚、抗菌などに利用される酸化チタン含有光触媒塗布液及びその製造方法並びに当該塗布液を用いた酸化チタン光触媒構造体に関し、特に塗布時の膜のひび割れが少なく、厚膜にしても透明性の高い膜を与える酸化チタン含有光触媒塗布液及びその製造方法に関する。

## 【0002】

【従来の技術】 酸化チタン光触媒は、紫外線を吸収して起こる化学反応により、 $\text{NO}_x$ などの有害物質除去、脱臭、防汚、抗菌などの効果を示すことで知られている。ところで、光触媒効果を工業的に発現させるためには基材上に光触媒薄膜を担持させることが必要である。ガラス、金属、セラミクス、各種プラスチックなどの基材表面に酸化チタンを付与する方法として、酸化チタン前駆体であるチタンアルコキシド、有機酸チタン、塩化チタンなどのチタン塩などを塗布し、焼き付ける方法、酸化

チタン粉体やゾルとバインダーの混合物を塗布する方法などがある。この様な光触媒構造体を製造する場合、酸化チタン薄膜は厚い方が効果が高いが、膜厚を厚くすると、酸化チタンを含む膜は白濁化するため、透明性を必要とする用途では、なかなか厚膜を利用することは困難であった。そこで透明性を得るために50nm以下の微粒子の酸化チタンを使用すると透明膜は形成しやすいものの、50nm以下の酸化チタンを用いて1 $\mu\text{m}$ を越えるような膜厚を得ようとする、成膜時に膜がひび割れやすくなる。ひび割れは外観的に問題があるだけでなく、膜の基材に対する密着性の低下を引き起こし、膜の一部が脱落し、光触媒効果を持続させることができない。このひび割れは、塗布液中にひび割れの原因である収縮応力を緩和するための材料を添加したり、塗布液と基材の間に応力を緩和する層を別に設けることにより防止をすることはできるが、いずれの方法も光触媒活性を低下させたり、製造コストが増大するなど根本的な解決方法としては不十分であった。

## 【0003】

【発明が解決しようとする課題】 光触媒として使用する酸化チタンの粒子径を大きくすることは、ひび割れ防止に効果があることがわかっているが、粒子径の増大は、透明性の低下と直結しており、高い透明性の確保と、膜のひび割れ防止を両立させることは、二律背反で大きな課題であった。本発明はこれらの問題を酸化チタンの物性とアルコール量を検討することにより解決したものである。

## 【0004】

【課題を解決するための手段】 即ち、本発明は基材上に酸化チタンを主成分とする薄膜を形成させる塗布液において、平均粒子径が50nm～120nm、結晶粒子径6～18nmの酸化チタン( $\text{TiO}_2$ )を0.1～10重量%、シリカ化合物( $\text{SiO}_2$ )を0.1～10重量%、アルコール溶媒を60重量%以上含むことを特徴とする酸化チタン含有光触媒塗布液及びその製造方法に関する。更にまた、本発明は当該塗布液を用いた高い触媒活性と実用的な膜強度を有する酸化チタン透明薄膜担持光触媒構造体に関する。

## 【0005】

【発明の実施の形態】 以下、本発明を詳細に説明する。本発明において使用される酸化チタンは、平均粒子径50nm～120nmの粒子、より好ましくは70nm～100nmの粒子である。平均粒子径は、レーザーを利用した散乱法によって測定できる。平均粒子径が50nm未満の粒子では、塗膜の透明性は高くなるが、成膜時にひび割れやすくなるため、膜厚を増加させることが困難である。一方、平均粒子径が120nmより大きい場合は、元来酸化チタンは白色顔料であるため、隠蔽性が高く、塗膜を白濁化する。また、塗布液組成によっては、保管中に沈殿物を生成する可能性がある。

【0006】 本発明の酸化チタンはアナターゼ型酸化チ

タンを主成分とするものであるが、若干のルチル型酸化チタンが混在していてもよい。ところで、本発明の塗布液中には結晶子径6nm~18nm、更に好ましくは8nm~12nmの酸化チタンが0.1~10重量%含まれていることが必要である。即ち、結晶子径が6nm未満では光触媒効果が充分でない場合があるだけでなく、このような微結晶は膜のひび割れの原因となる。また18nmを上廻ると、それに伴って酸化チタンの平均粒子径も大きくなり、厚膜にすると白濁し、透明性を必要とする用途に適應できない。

【0007】ところで、このような平均粒子径及び結晶子径を有する酸化チタンは塗布液を製造する際にいかなる方法でこれを導入しても良いが、塗布液中で沈殿や凝集を起こすことなく均一に分散していることが必要である。

【0008】粉体の酸化チタンを塗布液中に均質に分散することは困難であるため、好ましくは酸化チタンゾルの方法で導入することが望ましい。酸化チタンゾルの製造方法は特に限定されないが、平均粒子径や結晶子径を自由に制御できる製造方法が好ましい。

【0009】この様な酸化チタンの製造方法としては、粉末のアナターゼ型酸化チタンを酸やアルカリの存在下で解こうさせてもよいし、粉碎によって粒子径を制御しても良い。また、硫酸チタンや塩化チタンを熱分解あるいは中和分解して得られる含水酸化チタンを物理的、化学的方法で結晶子径、粒子径の制御を行っても良い。ゾル溶液中での分散安定性を付与するために、分散安定剤を使用してもよい。

【0010】分散安定剤としては、特に限定されることなく各種の分散安定剤が使用できるが、酸性またはアルカリ性の分散安定剤が好ましく使用される。酸性の分散安定剤としては硝酸、塩酸などの鉱酸、カルボン酸、オキシカルボン酸、ポリカルボン酸などの有機酸などが挙げられる。アルカリ性の分散安定剤としてはカルボン酸、ポリカルボン酸類のアルカリ金属塩やアンモニア、1~4級のアミン類およびそれらにヒドロキシ基を付加したアルカノールアミン類が好例として挙げられる。これら分散安定剤は単独または併用して使用することができる。酸性とアルカリ性の分散剤を同時に用いることもできる。分散安定剤として有機酸を使用すると、後述する有機溶媒との混和性が良好であることに加えて、pHが極端に低下せず且つ製造時に使用する設備を腐食しにくいので特に好ましい。有機酸の種類としては酢酸、シュウ酸、グリコール酸、乳酸、酒石酸、リンゴ酸、クエン酸などが特に好ましい。有機酸の量は、塗布液中に於いて0.005~5重量%で有ることが好ましく、酸化チタンゾル製造時にこれを含有させても良いし、一部を塗布液調製時に添加しても良いが概して全社の態様が望ましい。0.005重量%未満であると、酸化チタンが凝集して沈降し易くなり、5重量%よりも多いと塗膜中に有機酸が残存して塗膜の密着性、透明性を阻害する。また、有機酸を

利用しても塗布液のpHは2以上に調整されるべきである。pHが2以下になると金属を腐食させる恐れがある。

【0011】さて、本発明に於いて使用する前記酸化チタンの塗布液中に於ける濃度は $TiO_2$ として0.1~10重量%であるように調製される。塗布液中の濃度が0.1重量%未満であると一回塗りでは塗膜の膜厚が薄く、重ね塗りが必要であり経済的ではない。一方、10重量%を越える場合は塗布液の粘度が高くなり、ハンドリング性が悪くなるため好ましくない。より好ましくは1~5重量%が選択される。

【0012】本発明のシリカ化合物としては、アルコキシシラン、あるいはアルコキシシラン類の縮合物、加水分解物、シリコンワニス等が使用できる。3官能のアルコキシシランは一般的にはシランカップリング剤と呼ばれることも多いが、本発明ではシリコン1分子に1つ以上のアルコキシ基が結合している化合物をアルコキシシランと称する。具体的に例示すると4官能アルコキシシランとしてはテトラメトキシシラン、テトラエトキシシラン、テトラプロポキシシラン、3官能のアルコキシシランとしてはメチルトリメトキシシラン、メチルトリエトキシシラン、フェニルトリメトキシシラン、フェニルトリエトキシシラン、ビニルトリメトキシシラン、ビニルトリエトキシシラン、メタクリロキシプロピルトリメトキシシラン、グリシドプロポキシトリメトキシシラン、グリシロプロピルメチルジエトキシシラン、アミノプロピルトリエトキシシラン、アミノエチルアミノプロピルトリメトキシシラン、メルカプトプロピルトリメトキシシラン、2官能のアルコキシシランとしてはジメチルジメトキシシラン、ジメチルジエトキシシラン、ジフェニルジメトキシシラン、ジフェニルジエトキシシランなどがある。縮合物としてはシリケート40、シリケート48、シリケート51等の4官能アルコキシシランの縮合物が挙げられる。

【0013】また加水分解物としてはアルコキシシラン類を有機溶媒と水及び触媒を使用して加水分解させたものが使用できる。これらのシリカ化合物の内、特にテトラメトキシシラン、テトラエトキシシラン、シリケート40、シリケート48、シリケート51およびそれらの加水分解生成物であるアルコール性シリカゾルは、膜を強固に基材上に固定でき、且つ比較的安価であることから特に好適である。

【0014】上記アルコール性シリカゾルの製造方法は特に限定されることはなく、塗布液中でアルコキシシランの加水分解反応を行っても良いし、アルコキシシランを加水分解または部分加水分解し、既にアルコール性シリカゾルとなったものを酸化チタン液に添加しても良い。本発明に於いてはシリカ化合物を塗布液中に $SiO_2$ として0.1~10重量%、より好ましくは1~5重量%含ませることによって密着性の優れた塗膜を形成することができる。シリカ化合物含有量が0.1重量%未満では、塗膜の

密着性が極端に悪化し、好ましくない。また10重量%以上では塗布液の粘度が高くなりハンドリング性が悪くなるばかりでなく、塗布液が保管中に温度の影響でゲル化する場合がある。

【0015】これらのシリカ化合物は酸化チタンと混合して塗布液に調製されるが、両者の調整のみでは上記条件を満足させても本発明の目的を達成することはできない。本発明の目的を達成させるためには上記条件に加えてアルコール溶媒を使用することである。使用するアルコール溶媒としてはメタノール、エタノール、プロパノール、ブタノールなどの一価低級アルコール、エチレングリコール、プロピレングリコールなどの多価アルコール類およびそれらのエステルであるセルソルブなどが好例として挙げられる。これらアルコール溶媒の量は塗布液中60重量%以上である。60重量%未満では、高い透明性を有し、ひび割れの少ない厚い塗膜を得ることはできない。

【0016】本発明の塗布液の製造方法については、特に限定されることはないが、例えば、上記の酸化チタン、シリコン化合物、アルコール溶媒を所定の割合で混合することにより容易に製造することができる。混合の順序も任意で良く、全成分が均質に混合されるまで攪拌する。塗布液の調整は光触媒構造体を作成する直前即ち、各種基材に本発明塗布液を塗布する直前でもよいし、塗布液として保管して於いてもよい。光触媒構造体を作成する設備の都合などによりpHを調整する必要性がある場合は、塗布液製造時、または塗布直前に酸またはアルカリで所望のpHに調整することもできる。本発明の塗布液のpH調整には、上述の有機酸、アミン類が特に好ましくpH2~12の範囲で任意の値に調整される。pH2以下では設備を腐食させる可能性があるので好ましくない。また、pH12以上では酸化チタンやシリカ化合物が沈殿したり、塗布液が極端に増粘したりするので好ましくない。酸化チタンゾルを使用する場合は、酸化チタンゾルの調整時に事前にpHを調整しておくこともできる。

【0017】本発明塗布液は、タイルや瓦、ガラス等のセラミクス類、鉄、アルミ等の金属類、アクリル、PET、ポリカーボネート、塩ビ等のプラスチック類、各種の塗装表面やコンクリート、モルタル表面、布、紙などに塗布し光触媒構造体とすることができる。

【0018】基材形状は板状、フィルム状、成型体などいずれでも可能である。塗布液を基材上に塗布して酸化チタン薄膜を形成させる方法としては、刷毛塗り、スプレー塗布、スピコート、ディップコート、ロールコート、グラビアコート、バーコートなど各種の塗布方法を基材の形状を考慮して選択できる。塗布液の乾燥は基材の種類によって異なるが、通常300℃以下で熱処理される。ガラスやセラミクスを基材とする場合は、高い温度で処理する方が塗膜の基材に対する密着性が良くなる。しかしながら600℃以上では酸化チタンの焼結による比

表面積の低下が著しく、触媒効果が低下する。また、基材が、アクリル、PET、ポリカーボネート、塩化ビニルなどのプラスチック類の場合は基材の耐熱性から熱処理温度は150℃以下となる。酸化チタン薄膜の膜厚は厚い程触媒効果は高くなるが、5 $\mu$ m以上になると膜厚の増加と触媒効果は必ずしも比例しなくなるので、これ以上の膜厚は一般的には経済的でない。また膜厚があまりに厚いとひび割れの可能性があるので、実用的には0.2~5 $\mu$ m程度である。

10 【0019】塗膜形成にあたり、プラスチック類や金属を基材とする場合は、基材と酸化チタン薄膜との密着性を更に一層高めるために、基材と酸化チタン薄膜との間に接着層を設けることができる。接着層としては基材と酸化チタン薄膜組成の両方に親和性の高いものが好ましく、アクリル樹脂とシリコンを同時に含むものは、密着性の高い強靱な接着層を形成でき、本発明塗布液によって形成される光触媒層のひび割れ防止に優れた効果を発現し特に好適である。接着層は上記成分を含む塗料組成物を本発明塗布液と同様の方法で塗布することによって容易に形成させることができる。接着層の膜厚は限定されないが、0.2 $\mu$ m程度以上であれば十分な密着性を付与できる。本発明に於ける接着層を形成する塗料組成物としては上記の通りアクリル樹脂とシリコンを同時に含むものが望ましく、塗料組成物中のシリコン含有量は、SiO<sub>2</sub>換算で、全乾燥固形分量に対して5~50重量%であることが好ましい。この範囲が最も高い密着力とひび割れ防止効果を発揮する。このシリコン含有量(SiO<sub>2</sub>)の測定方法はJIS K 5400-8に記載の加熱残分中の灰分の測定方法に準じて測定する。

30 【0020】上記の接着層形成の塗料組成物は、例えばシリカゾルやシリコーン樹脂、アルコキシランなどの有機シリコン化合物をアクリル樹脂溶液に混合することにより容易に製造することができる。また、アクリル樹脂に替えて、あるいはアクリル樹脂とともにアクリル分子内に共有結合でシリコンを含むアクリル変性シリコン樹脂、シリコン変性アクリル樹脂も使用できる。塗料組成物製造の溶媒としてはトルエン、キシレン、ケトン、アルコールなどが挙げられるが水系のエマルジョンタイプでもよい。本発明の酸化チタン含有光触媒塗布液は、  
40 以上詳記したように構成されているから、これを各種基材に塗布したときは高い透明性を有するひび割れの少ない高性能の光触媒塗膜を形成させることができる。

【0021】

【実施例】以下に、これまで述べてきた発明の詳細を具体的に例を挙げて説明するが、本発明はそれらの実施例によって限定されるものではない。また特に断らない限り%は全て重量%を示す。

【0022】(実施例1) TiO<sub>2</sub>6%の多木化学(株)製酸化チタンゾルA-6を酸化チタン(TiO<sub>2</sub>)含有量が3.5%になるまでイオン交換水で希釈した後、140℃で5h水熱処理

した。このゾル液にpH3.0になるまでクエン酸1水和物を加えた後、限外濾過膜を用いて洗浄、濃縮し、結晶子径10.2nm、平均粒子径82nmの酸化チタンを15%、クエン酸1.5%を含有するpH3.3の乳白色ゾル(A)を得た。このゾル(A)333部にエタノール616部、キシダ化学(株)製テトラメチルシリラン( $\text{SiO}_2=39.5\%$ )51部を添加混合して、酸化チタン含有量5%、シリカ化合物( $\text{SiO}_2$ )含有量2%、アルコール溶媒量62%、クエン酸含有量0.5%の本発明光触媒塗布液を得た。この塗布液のpHは4.2、粘度は3.6mPa・sで、乳白色のコロイド溶液であった。この液を40cm<sup>2</sup>のガラス板に乾燥重量が約6mg(厚さ0.5μm)となるようにスピンコーティングし、本発明光触媒構造体を得た。この光触媒膜は透明であり、日本電色工業(株)製COH-300Aで測定した膜のヘイズ率は0.7%であった。

【0023】(実施例2) 5L反応容器に、γ-メタクリロキシプロピルトリメチルシリラン10部、メタクリル酸2-ヒドロキシエチル5部、メタクリル酸メチル17.5部、アクリル酸n-ブチル10部、スチレン7.5部、キシレン47部、t-ブチルパーオキシ-2-エチルヘキサノエート3部を入れ常法により重合させた。得られた樹脂100重量部、MKSメチルシリケートMS-56(三菱化学(株)社製テトラメチルシリケート部分加水分解物縮合物、nの平均値=10)50重量部、ジブチルスズラウリレート1重量部、キシレン700重量部、イソプロピルアルコール150重量部を別の5L反応容器に入れ混合、攪拌して、接着層塗料組成物を調製した。この塗料組成物中のシリコン含有量は、全乾燥固形分量に対して38%( $\text{SiO}_2$ )であった。この接着層用塗料組成物を40cm<sup>2</sup>のアクリル板に乾燥重量が10mgとなるようにスピンコーティングし、さらに実施例1で得た本発明光触媒塗布液を乾燥重量が約6mg(厚さ0.5μm)となるようにスピンコーティングし、本発明光触媒構造体を得た。この光触媒膜は透明であり、日本電色工業(株)製COH-300Aで測定した膜のヘイズ率は0.7%であった。

【0024】(実施例3) 実施例2で得られた接着層用塗料組成物を40cm<sup>2</sup>のアクリル板に乾燥重量が10mgとなるようにスピンコーティングし、さらに実施例1で得た本発明光触媒塗布液を乾燥重量が約12mg(厚さ1.0μm)となるようにスピンコーティングし、本発明光触媒構造体を得た。この光触媒膜は透明であり、ヘイズ率は1.0%であった。

【0025】(実施例4) 多木化学(株)製酸化チタンゾルA-6に酸化チタン( $\text{TiO}_2$ )に対するモル比0.5のアンモニアをアンモニア水溶液として加え、さらにイオン交換水を加えて酸化チタン( $\text{TiO}_2$ )含有量を3.5%に調整した。この液を145℃で5h水熱処理した。この液にリンゴ酸をpH2.6になるまで加えてさらに120℃で3h水熱処理した後、リンゴ酸を添加しながら限外濾過膜を用いて洗浄、濃縮し、結晶子径14.8nm、平均粒子径93nmの酸化チタンを10%、リンゴ酸を0.7%含有するpH3.0の乳白色ゾルを

得た。このゾル250部に多摩化学工業(株)製エチルシリケート40( $\text{SiO}_2=40\%$ )16部、メタノール50部、エタノール650部、イオン交換水33、シュウ酸2水和物1部を混合して酸化チタン含有量2.5%、シリカ化合物( $\text{SiO}_2$ )含有量0.64重量%、アルコール溶媒量70%、有機酸含有量0.2%の本発明光触媒塗布液を得た。この塗布液のpHは3.8、粘度は3.1mPa・sで、白色のコロイド溶液であった。この液を40cm<sup>2</sup>のガラス板に乾燥重量が約6mg(厚さ0.5μm)となるようにスピンコーティングし、本発明光触媒構造体を得た。この光触媒膜は干渉色を伴った透明膜であり、日本電色工業(株)製COH-300Aで測定したヘイズ率は1.1%であった。

【0026】(実施例5) 実施例2で得られた接着層用塗料組成物を40cm<sup>2</sup>のアクリル板に乾燥重量が10mgとなるようにスピンコーティングし、さらに実施例1で得た光触媒塗布液を乾燥重量が約6mg(厚さ0.5μm)となるようにスピンコーティングし、本発明光触媒構造体を得た。この光触媒膜は透明であり、ヘイズ率は1.1%であった。このアクリル板2枚を1.9L容のセパラブルフラスコに入れて、濃度100ppmとなるようアセトアルデヒドを導入し、膜表面で1mW/cm<sup>2</sup>の紫外線強度になるようにブラックライトを90分照射したところ、容器内のアセトアルデヒド濃度は26ppmまで低下していた。

【0027】(実施例6) 実施例2で得られた接着層用塗料組成物を40cm<sup>2</sup>のアクリル板に乾燥重量が10mgとなるようにスピンコーティングし、さらに実施例1で得た光触媒塗布液を乾燥重量が約12mg(厚さ1.0μm)となるようにスピンコーティングし、本発明光触媒構造体を得た。この光触媒膜は透明であり、ヘイズ率は1.5%であった。このアクリル板2枚を1.9L容のセパラブルフラスコに入れて、濃度100ppmとなるようアセトアルデヒドを導入し、膜表面で1mW/cm<sup>2</sup>の紫外線強度になるようにブラックライトを90分照射したところ、容器内のアセトアルデヒド濃度は8ppmまで低下していた。

【0028】(実施例7) 実施例1で製造した酸化チタンゾル(A)に2-アミノエタノールを添加してpH11に調整した後、再び限外濾過膜で洗浄して酸化チタン( $\text{TiO}_2$ )濃度15%、pH9.3の乳白色ゾル(B)を得た。このゾル(B)の酸化チタンの結晶子径は10.2nm、平均粒子径は75nmであった。ゾル(A)に代えてゾル(B)を使用し実施例1と同じ方法により乳白色の本発明光触媒塗布液を調製した。この液を40cm<sup>2</sup>のガラス板に乾燥重量が約6mg(厚さ0.5μm)となるようにスピンコーティングし、本発明光触媒構造体を得た。この光触媒膜は干渉色を伴った透明膜であり、日本電色工業(株)製COH-300Aで測定したヘイズ率は0.8%であった。

【0029】(比較例1)  $\text{TiO}_2$ 6%の多木化学(株)製酸化チタンゾルM-6を酸化チタン( $\text{TiO}_2$ )含有量が4.0%になるまでイオン交換水で希釈し、クエン酸でpH2.5に調整した後、140℃で3h水熱処理した。得られたゾル液を限

外濾過膜を用いて洗浄した後、加熱濃縮し、結晶子径5.0nm、平均粒子径8nmの酸化チタンを15%、有機酸2.5%含有するpH3.3の淡黄色ゾル(C)を得た。このゾル(C)333部にエタノール616部、キシダ化学(株)製テトラメトキシシラン( $\text{SiO}_2=39.5\%$ )51部を混合して、酸化チタン( $\text{TiO}_2$ )含有量5%、シリカ化合物( $\text{SiO}_2$ )含有量2%、アルコール溶媒量62%、有機酸含有量0.8%の光触媒塗布液を得た。この塗布液のpHは4.5、粘度は5.0mPa・sで、淡黄色のコロイド溶液であった。この液を40cm<sup>2</sup>のガラス板に乾燥重量が約6mg(厚さ0.5μm)となるようにスピンコーティングし、光触媒構造体を作成しようとしたが、乾燥時にひび割れし、成膜できなかった。

【0030】(比較例2) 多木化学(株)酸化チタン粉末(A-100)( $\text{TiO}_2=86\%$ )100部、関東化学(株)製リンゴ酸16部、イオン交換水228部を混合した後、ピーズミルで粉碎し、結晶子径6nm、平均粒子径400nmの酸化チタンを25%含有するpH2.3の白色ゾル(D)を得た。このゾル(D)200部にエタノール616部、キシダ化学(株)製テトラメトキシシラン( $\text{SiO}_2=39.5\%$ )51部、イオン交換水133部を混合して、酸化チタン( $\text{TiO}_2$ )含有量5%、シリカ化合物( $\text{SiO}_2$ )含有量2%、アルコール溶媒量62%の光触媒塗布液を得た。この塗布液のpHは3.9、粘度は3.3mPa・sで、白色のコロイド溶液であった。この液を40cm<sup>2</sup>のガラス板に乾燥重量が約6mg(厚さ0.5μm)となるようにスピンコーテ

ィングし、光触媒構造体を得た。この光触媒膜はやや濁った膜であり、日本電色工業(株)製COH-300Aで測定したヘイズ率は2.8%であった。

【0031】(比較例3)  $\text{TiO}_2$ 6%の多木化学(株)製酸化チタンゾルA-6を酸化チタン含有量が4.0%になるまでイオン交換水で希釈した後、130℃で5h水熱処理した。このゾル液にpH3.0になるまでクエン酸を加えた後、限外濾過膜を用いて洗浄、濃縮し、結晶子径9.2nm、平均粒子径52nmの酸化チタンを15%含有するpH3.3の乳白色ゾルを得た。このゾル333部にエタノール300部、キシダ化学(株)製テトラメトキシシラン( $\text{SiO}_2=39.5\%$ )51部、イオン交換水316部を混合して、酸化チタン( $\text{TiO}_2$ )含有量5%、シリカ化合物( $\text{SiO}_2$ )含有量2%、アルコール溶媒量30%、有機酸含有量0.5%の光触媒塗布液を得た。この塗布液のpHは4.0、粘度は3.0mPa・sで、乳白色のコロイド溶液であった。この液を40cm<sup>2</sup>のガラス板に乾燥重量が約6mg(厚さ0.5μm)となるようにスピンコーティングし、光触媒構造体を得た。膜の周辺部にクラックが発生して膜が剥離した。

【0032】

【発明の効果】本発明は光触媒として使用する酸化チタンの粒子径を大きくしても、ひび割れ防止に効果があり、高い透明性が確保された酸化チタン含有光触媒塗布液及びその製造方法である。

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